

# A hierarchical research by large-scale and *ab initio* electronic structure theories – Si and Ge cleavage and stepped (111)-2×1 surfaces –

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## Abstract

The *ab initio* calculation with the density functional theory and plane-wave bases is carried out for stepped Si(111)-2×1 surfaces that were predicted in a cleavage simulation by the large-scale (order- $N$ ) electronic structure theory (T. Hoshi, Y. Iguchi and T. Fujiwara, Phys. Rev. B **72** (2005) 075323). The present *ab initio* calculation confirms the predicted stepped structure and its bias-dependent STM image. Moreover, two (meta)stable step-edge structures are found and compared. The investigation is carried out also for Ge(111)-2×1 surfaces, so as to construct a common understanding among elements. The present study demonstrates the general importance of the hierarchical research between large-scale and *ab initio* electronic structure theories.

*Key words:* order- $N$  calculation; density functional theory; cleavage; Si(111)-2×1 surface; bias-dependent STM image.

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## 1. Introduction

A promising theoretical approach to nano materials is a hierarchical or multiscale research by large-scale and *ab initio* electronic structure calculations, since the research can handle, seamlessly, nano systems with a wide range of length scale. Nowadays, several *ab initio* calculation methods are well established, typically, for systems with  $10^1 - 10^2$  atoms and a popular method is the one with the density functional theory and plane-wave bases (DFT-PW calculation) (1). Electronic structure methods for larger systems, on the other hand, have been proposed by many groups. A set of fundamental methodologies of large-scale calculation and related theories were developed.

(2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15; 16; 17; 18) Among them, the large-scale calculations were realized by ‘order- $N$ ’ algorithms and/or parallel computations. Samples with  $10^2$ - $10^7$  atoms were calculated with tight-binding form Hamiltonians. Now the program code has the name of ‘ELSES’ (=Extra-Large-Scale Electronic Structure calculation; <http://www.elses.jp/>) . The code was used particularly in the researches of silicon cleavage (explained hereafter), helical multishell gold nanowires (12; 16; 17) (See Ref. (19) as experiments) and nano-polycrystalline diamond (18) (See Ref. (20) as experiments). Other methodologies for large-scale calculations can be found, for example, in the literatures of Refs. (10; 15).

The present paper focuses on the cleavage dynamics and resultant stepped Si(111)-2x1 surfaces, as a hierarchical research by the large-scale calculations and the DFT-PW calculations. This paper organized as follows; Section 2 is devoted to a review of the Si(111)-2x1 surface and the result of the large-scale calculations in previous papers. In Sec. 3, the results of DFT-PW cal-

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culations are presented for stepped Si and Ge(111)-2 $\times$ 1 surfaces, so as to construct a hierarchical research. Finally, a summary is given.

## 2. Si(111)-2 $\times$ 1 cleavage mode and its large-scale calculations

The Si(111)-2 $\times$ 1 surface, called Pandey structure, (21) appears on cleaved samples and is of great importance in fracture science and surface science. See papers (23; 24; 22; 25; 26; 27; 7; 29; 28) and references therein. In the Pandey structure, threefold-coordinated surface atoms form a zigzag chain, like a part of graphen sheet. The zigzag chains on the surface are tilted and a pioneering DFT-PW calculation shows the transformation process between the two tilted structures. (24) Cleaved Ge samples also contain the (111)-2 $\times$ 1 surface. See the above papers and reference therein.

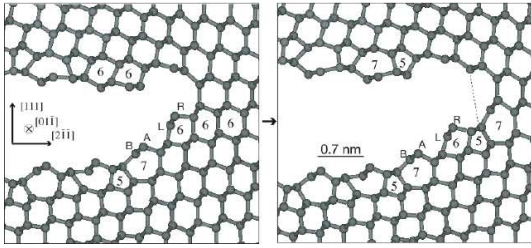


Fig. 1. Close up of the snapshots the cleavage dynamics with a 10-nm-scale system, by the large-scale electronic structure calculation. (7) A step is formed on the (111)-2 $\times$ 1 surface. The time interval between the left and right snapshots is 0.6 ps. See the text for details. Several five-, six-, seven-membered rings are marked as ‘5’, ‘6’ and ‘7’, respectively. The dashed lines indicate the initial (crystalline) bonds.

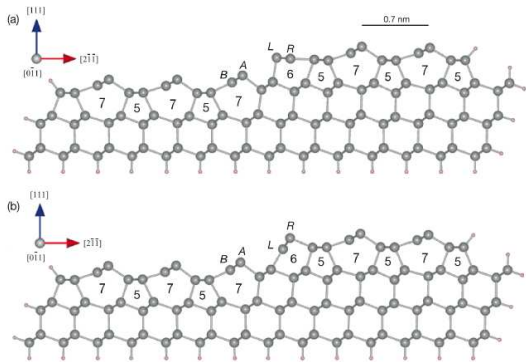


Fig. 2. Stepped Si(111)-2 $\times$ 1 structures calculated by the DFT-PW calculation. The small balls are hydrogen terminations. (a) ‘L-type’ and (b) ‘R-type’ step-edge structures are obtained as stable structures. See the text for details.

Large-scale order- $N$  calculations were carried out for the cleavage dynamics and the local electronic density

of states (LDOS) on the resultant cleaved surface. (4; 7; 9; 10; 11) The cleavage dynamics was carried out by the generalized Wannier-state method (2; 3; 4; 5; 7; 9; 10; 11) and the LDOS calculation was realized by a Krylov-subspace algorithm for the Green’s function. (6; 9; 8)

Figure 1 shows an example of the cleavage dynamics with a 10-nm-scale sample or  $10^4$  atoms. (7) The (111)-2 $\times$ 1 reconstruction appears on the cleaved surface. Several results contain step formations on the (111)-2 $\times$ 1 surface, as shown in Fig. 1. In Fig. 1, several five-, six-, seven-membered rings are marked as ‘5’, ‘6’ and ‘7’, respectively, as a guide for eye. The 2 $\times$ 1 reconstruction appears, when the two successive six-membered rings are transformed into a set of five- and seven-membered rings. A characteristic six-membered ring appears at the step-edge region.

Surface atoms on the flat region, form tilted zigzag chains of threefold-coordinated atoms, as explained in the first paragraph of the present section. For example, the *A* atom in Fig. 1 is placed on the vacuum-side (upper) region and the *B* atom is placed on the bulk-side (lower) region. The zigzag chain with the reverse tilting is also obtained. It is remarkable that the surface atoms at the step-edge region, marked as ‘*L*’ and ‘*R*’, also form a zigzag chains of threefold-coordinated atoms, as on the flat region. One can consider, therefore, that the two tilted structures may be stable at the step-edge region, as on the flat region, although the simulation results contain only one tilted structure in which the *R* atoms is placed on the vacuum-side region and the *L* atoms is on the bulk-side region. Moreover, the calculated LDOS indicates a bias-dependent image of the scanning tunnelling spectroscopy (STM) both on the flat region and the step-edge regions. The peaks in the LDOS profile are located at almost the same positions in the step-edge atoms, such as the *L* and *R* atoms, and the atoms on the flat region, such as the *A* and *B* atoms. A bias-dependent STM image was observed experimentally for the flat region. (22) The calculation predicts the same bias-dependent image on the step-edge region. The same step-edge structures and its bias-dependent STM image were suggested also for Ge cases, because of the similarity of electronic structure. (7)

## 3. *Ab initio* calculations

The properties of the stepped Si(111)-2 $\times$ 1 surface, predicted by the large-scale calculation, were confirmed by the DFT-PW calculation with a smaller sample. The Vienna *ab initio* simulation package (VASP) was used with the projector augmented wave method and the local density approximation. (30)

Figure 2 shows the calculated sample that contains 96 silicon atoms in the simulation cell. The sample corresponds to a ‘close up’ of the step-edge region of the large-scale calculation. The sample is periodic only in the  $[0\bar{1}1]$  direction, and the sample boundary is terminated by artificial hydrogen atoms.

Structures are optimized with several initial guesses and the two tilted step-edge structures in Fig. 2 are obtained as stable ones. The site names of  $A$ ,  $B$ ,  $L$  and  $R$  in Fig. 2 are consistent to those in Fig. 1. Hereafter, the structure in Fig. 2 (a) is called ‘L-type’ step-edge structure, since the  $L$  atom, the left atom of the step edge region, is located at the vacuum-side region and the  $R$  atom, the right atoms, is located at the bulk-side region. The structure in Fig. 2 (b) indicates the reverse tilting at the step-edge region and is called ‘R-type’ structure. The energy of the  $L$ -type structure is lower than that of the  $R$ -type structure by  $\Delta E \equiv E_R - E_L = 0.19$  eV per atom pair of the zigzag chain.

Additional calculations were carried out, so as to clarify physical discussions for the two step-edge structures. First, the structures were calculated with different tilting structures on the flat region, in which the zigzag chains on the flat region, such as the  $A$  and  $B$  atoms in Fig. 2, form the reverse tilting structure. The calculation result indicates that the above energy difference ( $\Delta E = 0.19$  eV) is independent on the tilting structures of the flat region and that the above energy difference stems from the local tilting structure of the step-edge region. Second, the energy difference was calculated also by the tight-binding form Hamiltonian used in the large-scale calculation and gives  $\Delta E = 0.22$  eV, which agrees satisfactorily with the above *ab initio* calculation.

Although the existence of the two stable structures at the step-edge regions is reasonable, as discussed in the previous section, it is interesting that the cleavage simulation of Fig. 1 contains the ‘R-type’ structure, the higher energy structure of the two. The appearance of the higher energy structure in the cleavage simulation can be understood, since the  $R$  atom is located on an upper position than the  $L$  atom, in an ideal diamond structure. The simulation realizes the dynamics with the time scale in 10 ps and it might be difficult to reproduce the transformation process from the ‘R-type’ structure into the ‘L-type’ one.

In Fig. 3, the STM images are calculated for the step-edge region of the ‘L-type’ structure. The calculation details are written in the caption. An occupied surface state is localized on the vacuum-side atom (the  $L$  atom) and an unoccupied surface state is localized on the bulk-side atom (the  $R$  atom). The calculated STM images for the flat region shows the same bias-dependency. These results are consistent to those of the large-scale calculation. Here it is noteworthy that the STM image for the ‘R-type’ structure should be

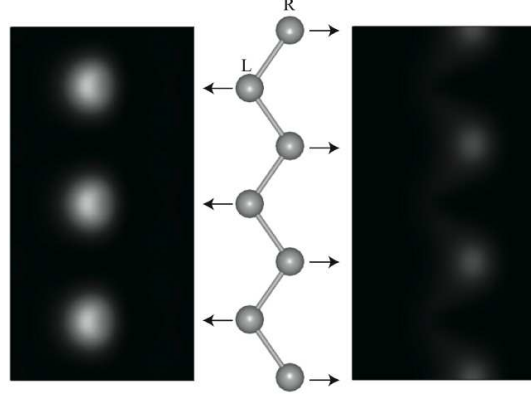


Fig. 3. The bias-dependent STM images at the step-edge atoms in the ‘L-type’ structure. The image was calculated with the DFT-PW calculation and the bias value  $\varepsilon_V$  is set to be  $\varepsilon_V = \varepsilon_F - 0.7$  eV and  $\varepsilon_F + 0.7$  eV in the left and right panels, respectively. The middle panel shows the top view of the zigzag chain of threefold-coordinated surface atoms, such as the  $L$  and  $R$  atoms in Fig. 2(a).

discussed more carefully, both in theory and experiment, since the height of the  $L$  and  $R$  atoms are different significantly, by approximately 1 Å. When STM images were calculated as the constant height calculations, like those for the ‘L-type’ structure in Fig. 3, and the probed height was set to be slightly higher than the  $R$  atom, the calculated images contain only the images for the  $R$  atom, like the right panel of Fig. 3, both for the positive and negative bias values, since the  $R$  atom is placed near the probed height.

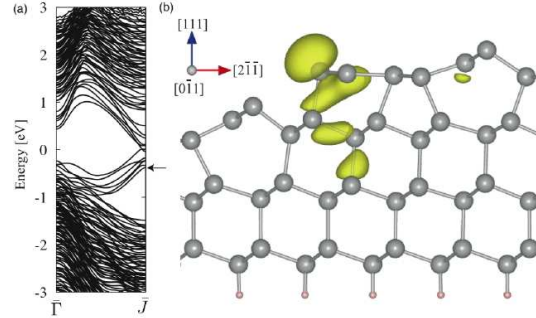


Fig. 4. (a) The band structure for the ‘L-type’ step-edge structure shown in Fig. 2(a). (b) The profile of the eigen state indicated by the arrow at the  $\bar{J}$  point in (a).

Figure 4 shows (a) the band structure and (b) a characteristic localized wavefunction for the ‘L-type’ step-edge structure. These results are quite similar to those of the flat Si(111)-2x1 surface, since the zigzag chain of threefold-coordinated atoms appears commonly in the two cases. The band structure of the flat Si(111)-2x1 surface is found, for example, in Ref. (26), in which they use the GW approximation, an advanced electronic structure theory beyond DFT. The surface states are

separated from the bulk bands at the  $\bar{J}$  point, as a common property among the band structures of the flat surface (Fig. 1 of Ref. (26)) and the stepped surface (Fig. 4(a)). Figure 4(b) shows a characteristic wavefunction localized at the step-edge region. The corresponding eigen level is placed at the lowest surface state level the  $\bar{J}$  point. The level is indicated by the arrow in Fig. 4(a). The wavefunction is a  $\pi$ -like state located on the vacuum-side ( $L$ ) atom at the step edge region and the same property is seen on the wavefunction on the flat surface (Fig. 2(a) of Ref. (26)). The energy gap between the occupied and unoccupied levels vanishes at the  $\bar{J}$  point in Fig. 4(a). It is speculated that the gap is underestimated artificially, as usually within DFT calculations, and a finite gap should appear in a real system, as that of Ref. (26)

The same investigation was carried out also for the stepped Ge(111)-2x1 surfaces. The energy of the  $L$ -type step-edge structure is lower than that of the  $R$ -type structure, as in the Si case. The energy difference between them is comparable to that in the Si case ( $\Delta E = 0.23$  eV). Therefore, the appearance of the stepped (111)-2x1 structure should be understood as a common property of the Si and Ge cases, which is consistent to the discussion in the previous section.

#### 4. Summary

A hierarchical research is presented for the stepped Si and Ge (111)-2x1 surface in the stable cleavage mode. The present DFT-PW calculation validates the predictions in our previous calculation with the large-scale order- $N$  theory (7) for (i) the stepped surface structure and (ii) its bias-dependent STM image.

The hierarchical research as a combined study of large-scale calculations with large (10-nm-scale) systems and finer calculations with smaller systems is general and is applicable to various nanomaterials, since all the theories are founded within a general framework of quantum mechanics for electron.

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